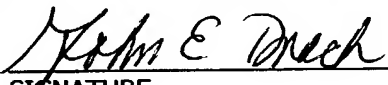


1C10 Rec'd PCT/PTO 1 8 MAR 2002

page 1 of 2

1010 Rec'd PCT/PTO 18 MAR 2002

| U.S. Application No. (If known, see 37 CFR 1.51)<br><b>10/088383</b>  | INTERNATIONAL APPLICATION NO.<br><b>PCT/EP00/08772</b>   | ATTORNEY'S DOCKET NUMBER<br><b>H 4193 PCT/US</b>   |              |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |
|---|--|--|--------------|--------------|---|----------|---|-------------|---|---------|--------------|--------------|--|--------------|----------|------------|-------------|--------------------|---------|---|-------------|--|---|--|------------|------|--------------------------------------|--------|--|------|-------------------|--------|---|------|-----------------------------|--------|---|------|------------------------------|--------|--|--|----------------------------|---------|----------|-----------------|
| <b>17. The following fees are submitted:</b><br><b>BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):</b><br>Neither international preliminary examination fee (37 CFR 1.482)<br>nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO<br>and International Search Report not prepared by the EPO or JPO..... <b>\$1,040.00</b><br><br>International preliminary examination fee (37 CFR 1.482) not paid to<br>USPTO but International Search Report prepared by the EPO or JPO..... <b>\$890.00</b><br><br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but<br>international search fee (37 CFR 1.445(a)(2)) paid to USPTO ..... <b>\$740.00</b><br><br>International preliminary examination fee paid to USPTO (37 CFR 1.482)<br>but all claims did not satisfy provisions of PCT Article 33(1)-(4) ..... <b>\$710.00</b><br><br>International preliminary examination fee paid to USPTO (37 CFR 1.482)<br>and all claims satisfied provisions of PCT Article 33(1)-(4)..... <b>\$100.00</b><br><br><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b> |  | <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="text-align: left;">CALCULATIONS</th> <th style="text-align: left;">PTO USE ONLY</th> </tr> <tr> <td><b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b></td> <td>\$ 890</td> </tr> <tr> <td>Surcharge of <b>\$130.00</b> for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30<br/>months from the earliest claimed priority date 37 (CFR 1.492(e)).</td> <td>\$ 0</td> </tr> <tr> <td> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <th style="width: 20%;">CLAIMS</th> <th style="width: 20%;">NUMBER FILED</th> <th style="width: 20%;">NUMBER EXTRA</th> <th style="width: 40%;">RATE</th> </tr> <tr> <td>Total Claims</td> <td>8 - 20 =</td> <td>0</td> <td>0 X \$18.00</td> </tr> <tr> <td>Independent Claims</td> <td>1 - 3 =</td> <td>0</td> <td>0 X \$84.00</td> </tr> <tr> <td>Multiple dependent claims (s)(if applicable)</td> <td>0</td> <td></td> <td>+ \$280.00</td> </tr> </table> </td> <td>\$ 0</td> </tr> <tr> <td><b>TOTAL OF ABOVE CALCULATIONS =</b></td> <td>\$ 890</td> </tr> <tr> <td>Reduction of 1/2 for filing by small entity, if applicable. 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| <b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>   | \$ 890   |  |              |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |
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| CLAIMS  | NUMBER FILED   | NUMBER EXTRA   | RATE         |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |
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| <b>TOTAL OF ABOVE CALCULATIONS =</b>  | \$ 890   |  |              |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |
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| <b>TOTAL FEES ENCLOSED =</b>  | \$ 890   |  |              |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |
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| a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed.<br><br>b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>50-1177</u> in the amount of <u>\$890.00</u> to cover the above fees.<br>A triplicate copy of this sheet is enclosed. Order No. <u>02-0138</u> .<br>c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any<br>overpayment to Deposit Account No. <u>50-1177</u> . A triplicate copy of this sheet is enclosed.<br><b>NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b))<br/>         must be filed and granted to restore the application to pending status.</b><br><br>SEND ALL CORRESPONDENCE TO: <b>Customer Label No. 23657</b>  |  |  |              |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |
| <br>SIGNATURE<br><br>John E. Drach<br>NAME ATTORNEY FOR APPLICANT<br>32,891<br>REGISTRATION NUMBER  |  |  |              |              |   |          |   |             |   |         |              |              |  |              |          |            |             |                    |         |   |             |  |   |  |            |      |                                      |        |  |      |                   |        |   |      |                             |        |   |      |                              |        |  |  |                            |         |          |                 |

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"Express Mail" mailing label number EL541614333US.

PATENT  
Docket No. H 4193 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

RE: PCT/EP00/08772  
International Filing Date: September 8, 2000  
Priority Date Claimed: September 17, 1999  
Applicant: Friesenhagen, et al.  
Title: METHOD FOR PRODUCING ALKYL-SUBSTITUTED BUTENOLS  
Applicants' Reference: H 4193 PCT/US

**PRELIMINARY AMENDMENT**

Commissioner for Patents  
Box PCT  
Washington, DC 20231

ATTN: DO/EO/US

Sir:

Before examination, in the national stage for the United States, of the above-captioned application under the Patent Convention Treaty, please amend as follows the translation supplied herewith of the application:

In the Specification:

*Please delete all text above line 8, of page 1, and replace the deleted matter with the following new section headings and new paragraph:*

**--TITLE OF THE INVENTION**

**Method for Producing Alkyl-Substituted Butenols**

**BACKGROUND OF THE INVENTION**

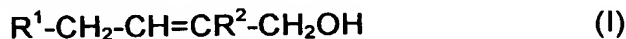
This invention relates to a process for the production of alkyl-substituted butenols by reduction of the corresponding aldehyde precursor in the presence of copper/zinc catalysts, the process being carried out continuously under isothermal conditions in a narrow temperature range.--

*On a separate, new page 16, following page 15, please add the following new section heading and paragraph containing an Abstract of the Disclosure:*

**Preliminary Amendment of U.S. National Stage for International Application  
PCT/EP00/08772 filed on September 8, 2000**

**--ABSTRACT OF THE DISCLOSURE**

Alkyl-substituted butenols having the formula (I):



wherein R<sup>1</sup> is a saturated or olefinically unsaturated alkyl or cycloalkyl group having from 4 to 16 carbon atoms and wherein R<sup>1</sup> is optionally substituted by an alkyl, cycloalkyl, aryl or alkaryl having up to 12 carbon atoms; R<sup>2</sup> is hydrogen or an alkyl group having from 1 to about 6 carbon atoms are produced by a process which comprises: (1) reacting an aldehyde of the formula (II):



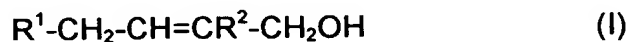
wherein R<sup>1</sup> has the same meaning as in formula (I), with the corresponding lower aldehyde to form an unsaturated aldehyde in an inert organic solvent; (2) continuously contacting an optionally calcined copper/zinc catalyst with the unsaturated aldehyde under isothermal conditions at temperatures of from about 45 to about 60°C and under a hydrogen pressure of from 1 to about 300 bar.--

In the claims:

Please cancel claims 1-9.

Please add the following new claims 10-17.

10. (New) A process for the production of alkyl-substituted butenols having the formula (I):



wherein R<sup>1</sup> is a saturated or olefinically unsaturated alkyl or cycloalkyl group having from 4 to 16 carbon atoms and wherein R<sup>1</sup> is optionally substituted by an alkyl, cycloalkyl, aryl or alkaryl having up to 12 carbon atoms; R<sup>2</sup> is hydrogen or an alkyl group having from 1 to about 6 carbon atoms the process comprising the steps of: (1) reacting an aldehyde of the formula (II):



wherein R<sup>1</sup> has the same meaning as in formula (I), with the corresponding lower aldehyde to form an unsaturated aldehyde in an inert organic solvent; (2) continuously contacting an optionally calcined copper/zinc catalyst

**Preliminary Amendment of U.S. National Stage for International Application  
PCT/EP00/08772 filed on September 8, 2000**

with the unsaturated aldehyde under isothermal conditions at temperatures of from about 45 to about 60°C and under a hydrogen pressure of from 1 to about 300 bar.

11. (New) The process of claim 10 wherein step (1) is carried out in a nonpolar organic solvent which can form an azeotrope with water.
12. (New) The process of claim 10 wherein step (1) is carried out in the presence of a catalyst which is an ammonium salt of an organic acid.
13. (New) The process of claim 10 wherein R<sup>2</sup> in formula (I) is a methyl group.
14. (New) The process of claim 10 wherein the lower aldehyde is propionaldehyde.
15. (New) The process of claim 14 wherein the propionaldehyde is used in a 2.5 to 10-fold molar excess based on the aldehyde of formula (II).
16. (New) The process of claim 10 wherein R<sup>1</sup> is a 4-(2,2,3-trimethylcyclopent-3-en-1-yl) group.
17. (New) The process of claim 10 wherein the organic solvent selected from the group consisting of toluene, xylene, benzene, cyclohexane and methyl cyclohexane.

**Preliminary Amendment of U.S. National Stage for International Application  
PCT/EP00/08772 filed on September 8, 2000**

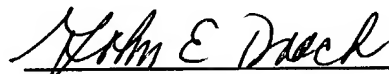
REMARKS

Claims 10-17 are currently pending in the instant application.

The Specification has been amended to include the preferred section headings pursuant to 37 C.F.R. §1. It is submitted that the amendments to the Specification made herein introduce no new matter. Their entry is therefore proper and respectfully requested. An Abstract of the Disclosure has been added on a separate sheet following the claims.

Original claims 1-9 have been canceled and replaced with new claims 10-17 solely for the purpose of improving clarity and grammar, which may suffer in translation, and not for any reason related to the statutory requirements for a patent. New claims 10-17 have not been added in response to any rejection, or in anticipation of any rejection related to the statutory requirements for a patent. Applicants respectfully submit that the scope of new claims 10-17 corresponds to the scope of original claims 1-9 and that new claims 10-17 are no narrower than original claims 1-9. Furthermore, although a moot point in view of their cancellation, Applicants respectfully submit that original claims 1-9 satisfied the requirements of 35 U.S.C. §112, as filed. New claims 10-17 are supported by the specification and no new matter has been introduced. Entry is therefore proper and respectfully requested. Prompt examination of the instant application in view of the amendments made herein is respectfully requested.

Respectfully submitted,



John E. Drach  
(Reg. No. 32,891)  
Attorney for Applicants  
(610) 278-4925

Cognis Corporation, Patent Dept.  
2500 Renaissance Boulevard, Suite 200  
Gulph Mills, PA 19406

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## Method for Producing Alkyl-Substituted Butenols

### Field of the Invention

This invention relates to a process for the production of alkyl-substituted butenols by reduction of the corresponding aldehyde precursor in the presence of copper/zinc catalysts, the process being carried out  
5 continuously under isothermal conditions in a narrow temperature range.

### Prior Art

Judging by demand, the availability of many natural perfumes is totally inadequate. From the perfumistic point of view, sandalwood oil is  
10 rated particularly highly and is of great value. It is obtained by steam distillation from the heartwood of the sandalwood tree, a tropical semiparasite which occurs in India and Malaysia. Heartwood appears after about 10 years and only begins to develop relatively quickly in 20-year-old trees. Fully grown trees are uprooted at the age of 30 to 60 because the  
15 roots are particularly rich in fragrant heartwood [cf. **E.T. Morris, Dragoco Report 1983 (30), 40**]. It will therefore be appreciated why perfume researchers are constantly endeavoring to develop suitable substitutes for natural sandalwood oil.

The focal points in the development of suitable substitutes for  
20 natural sandalwood oil were outlined by R.E. Naipawer in a review [in: **B.M. Lawrence, B.D. Mookherjee, B.J. Willis (Eds.): "Flavors and Fragrances: A World Perspective"**, Elsevier Publishers, Amsterdam 1988]. In this review, it is mentioned inter alia that, since the middle of the seventies, campholenyl derivatives have played an important part as  
25 synthetic perfumes with a sandalwood perfume. A key role in this access to synthetic sandalwood perfumes has been played by the fact that campholene aldehyde (B), the synthesis building block on which the

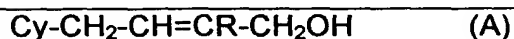
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PCT/EP00/08772

compounds mentioned are based, can readily be obtained from  $\alpha$ -pinene, a natural substance.

2-Alkyl-4-(2,2,3-trimethylcyclopent-3-enyl)-but-2-en-1-ols (A), hereinafter referred to as **sandalols**, are sought-after perfumes with a pronounced sandalwood fragrance.



Cy = 4-(2,2,3-trimethylcyclopent-3-en-1-yl) group

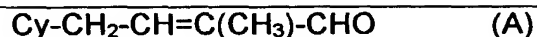
R = H or C<sub>1-6</sub> alkyl

**JP-A2-55/036423** (reported in **Chem. Abstr. 93/094886p**) describes a process for the production of such a sandalol in which  $\alpha$ -campholene aldehyde (B) is reacted with propionaldehyde (CH<sub>3</sub>-CH<sub>2</sub>-CHO) in the presence of sodium hydroxide as basic catalyst.



Cy = 4-(2,2,3-trimethylcyclopent-3-en-1-yl) group

The unsaturated aldehyde (C) formed in this mixed aldol condensation was isolated in a yield of 73.5%.



Cy = 4-(2,2,3-trimethylcyclopent-3-en-1-yl) group

Finally, in another step, this unsaturated aldehyde (C) was reduced with Al[OCH(CH<sub>3</sub>)]<sub>3</sub> to form the corresponding sandalol (A). The yield obtained is put at 85%.



DE-A-195 20 103 describes a process for the production of alkyl-substituted butenols where unsaturated aldehydes are prepared by aldol condensation in a first step and are subsequently reduced in the presence of an optionally calcined copper/zinc catalyst. Example 3 of this application  
5 (page 5, lines 5 to 26), which describes the second stage of the process (reduction step), refers to batch operation and a reaction temperature of 160°C.

Continuous operation in an extremely narrow and relatively low temperature range is neither disclosed nor suggested in DE-A-195 20 103.  
10 Isothermal operation is also not mentioned in DE-A-195 20 103.

### Description of the Invention

The known processes for the production of sandalols (A) are not entirely satisfactory in regard to yield and economy. Accordingly, there was  
15 a need for an improved process for the production of the compounds (A) and analogous compounds where the "Cy" group would be replaced by another saturated or olefinically unsaturated, optionally substituted alkyl or cycloalkyl group. More particularly, there was a need to ensure that the nonspecific formation of numerous secondary products would largely be  
20 avoided. Secondary products in a perfumistic context are understood to be worthless or even troublesome products.

It has now been found that alkyl-substituted butenols corresponding to general formula (I):



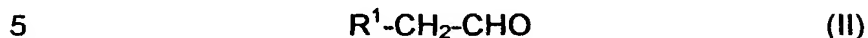
in which  $R^1$  is a saturated or olefinically unsaturated alkyl or cycloalkyl group containing 4 to 16 carbon atoms which may optionally be substituted by an alkyl, cycloalkyl, aryl or alkaryl group, with the proviso that this  
30 substituent contains at most 12 carbon atoms, and  $R^2$  is hydrogen or an

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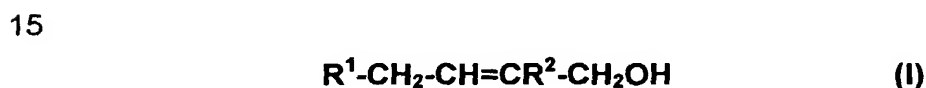
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alkyl group containing 1 to 6 carbon atoms,  
can be produced in high yields providing the aldol condensation of  
aldehydes corresponding to formula (II):



in which  $\text{R}^1$  has the same meaning as in formula (I), and the corresponding  
lower aldehyde is carried out in an inert organic solvent and the  
unsaturated aldehydes obtained are reduced in the presence of an  
10 optionally calcined copper/zinc catalyst, the process being carried out  
continuously under isothermal conditions in a narrow temperature range.

Accordingly, the present invention relates to a process for the  
production of alkyl-substituted butenols corresponding to general formula  
(I):



in which  $\text{R}^1$  is a saturated or olefinically unsaturated alkyl or cycloalkyl  
group containing 4 to 16 carbon atoms which may optionally be substituted  
20 by an alkyl, cycloalkyl, aryl or alkaryl group, with the proviso that this  
substituent contains at most 12 carbon atoms, and  $\text{R}^2$  is hydrogen or an  
alkyl group containing 1 to 6 carbon atoms,  
by reacting aldehydes corresponding to formula (II):



in which  $\text{R}^1$  has the same meaning as in formula (I), with the corresponding  
lower aldehydes and subsequently reducing the unsaturated aldehydes  
obtained,

30 i) the aldol condensation being carried out in an inert organic solvent

and

- (ii) the reduction of the unsaturated aldehydes being carried out in the presence of an optionally calcined copper/zinc catalyst, with the proviso that the reduction in step ii) is carried out continuously under isothermal conditions at temperatures of 45 to 60°C and under a hydrogen pressure of 1 to 300 bar.

The process according to the invention has the advantage over the prior art that intermediate products and valuable products are obtained in high purities and in substantially quantitative yields. In particular, it has the advantage that the valuable product (I) obtained in the hydrogenation step is formed with a very high chemical purity and selectivity. Of particular importance in this connection is the fact that unwanted secondary products, for example compounds derived from (I) of which the C=C double bonds are completely or partly hydrogenated, and unreacted aldehyde (from the aldol condensation), are formed in a distinctly reduced quantity by comparison with processes where the features to be observed in accordance with the invention do not exist. This is particularly of advantage when the valuable product (I) obtained in the hydrogenation step is used as a raw material for the production of perfumes.

#### Step i)

Particularly suitable inert organic solvents for step i) are nonpolar solvents which form an azeotrope with water. Examples of suitable solvents are toluene, xylene, benzene, cyclohexane and methyl cyclohexane.

In a special embodiment of the invention, ammonium salts of an organic acid are used to catalyze the aldol condensation.

Propionaldehyde is preferably used in a 2.5- to 10-fold molar excess, based on the aldehyde (II). In one particular embodiment, propionaldehyde is used in a 2.5- to 3.5-fold molar excess.

As already mentioned, the aldol condensation is preferably carried out in the presence of an ammonium salt of an organic acid in the process according to the invention. Basically, the nature of the acid is not critical. Nor does it matter whether the ammonium salt is used as such or whether  
5 it is formed in situ during the reaction - for example from an amine and an organic acid. Examples of suitable ammonium salts are benzyl trimethyl ammonium hydroxide, piperidiny acetate, pyrrolidinium acetate, ammonium acetate, dimethyl ammonium pyridiny acetate, morpholine acetate, Lewatit 11600 (active with acetic acid), piperidiny formate, N,N-tetraacetyl ethylenediamine, N,N-diacetyl ethylenediamine, dibutyl ammon-  
10 ium acetate and piperidiny propionate. The concentration of the catalyst is preferably in the range from 0.001 to 20 mole-% and more particularly in the range from 0.5 to 10 mole-%, based on the aldehyde (II) used.

In another preferred embodiment of the present invention, R<sup>1</sup> in  
15 general formula (I) is a 4-(2,2,3-trimethylcyclopent-3-enyl) group.

#### Step ii)

The process according to the invention is carried out at temperatures of 45 to 60°C. In one particularly preferred embodiment, the  
20 reaction temperature is in the range from 50 to 55°C.

The process according to the invention is distinguished inter alia by the fact that, in step ii), it is carried out both continuously and isothermally.

Carrying out the process according to the invention continuously in step ii), which is preferably carried out in a fixed-bed reactor, ensures that  
25 the proportion of secondary products is small. The reason for this on the one hand is that, where this procedure is adopted, it is readily possible by controlling the volumetric flow rate of aldehyde or aldehyde and solvent to keep the reaction time short. On the other hand, the heterogeneous catalysis applied here ensures that the reaction product is not  
30 accompanied by significant quantities of the catalyst.

Carrying out the process isothermally means that no significant temperature gradients occur in the continuously operated reactor and that, in particular, there are no temperature peaks. By contrast, a nonisothermal reaction procedure would be characterized by the occurrence of distinct temperature gradients or temperature peaks in the reactor. Nonisothermal conditions usually prevail in batch hydrogenation, i.e. hydrogenation in an autoclave. In continuous operation, a nonisothermal reaction procedure would be characterized by the absence of special precautions to control the exothermy of the reaction.

To establish isothermal conditions, a particular embodiment of the process according to the invention is characterized in that the temperature is controlled by external jacket heating, for example with thermal oil, and/or the throughflow rate is adjusted to a correspondingly high level.

In particular, the throughflow rate in step ii) is adjusted to a value of 0.5 to 1.5 m<sup>3</sup>/h and more particularly to a value of 0.8 to 1.2 m<sup>3</sup>/h.

A preferred embodiment of the invention is characterized in that the copper/zinc catalyst is used in particulate form, i.e. the catalyst which is used in the reaction zone of the fixed-bed reactor is in the form of solid particles (heterogeneous catalyst). The particles may assume various sizes and shapes, for example tablets, lumps, cylinders, rods, rings. Basically, the size of the particles is not critical. However, it is normally adapted to the particular reactor dimensions present so that the liquid phase and the carrier gas are able to pass through the reaction zone unhindered and no unwanted drop in pressure occurs in that region. Typical suitable particle sizes range from a mean diameter of ca. 1 millimeter to ca. 10 millimeters although larger or smaller particle sizes are also possible.

A typical laboratory apparatus for carrying out the process according to the invention comprises a fixed-bed reactor of a double-jacketed tube. The inner tube contains the heterogeneous hydrogenation catalyst and

acts as the reaction zone. The intermediate space is used for heating with a liquid medium. The aldehyde or the mixture of aldehyde and solvent can be delivered continuously to the reactor through heatable pipes by a controllable piston diaphragm pump. After leaving the reactor, the reaction  
5 products formed can readily be quantitatively removed via a cooling unit and an expansion system.

The typical technical equipment for carrying out the process according to the invention described with reference - by way of example - to a laboratory apparatus can readily be applied to correspondingly scaled  
10 up pilot-plant or production reactors. In principle, any of the usual tube or tube-bundle reactors may be used for this purpose.

So far as the hydrogen pressure is concerned, step ii) of the process is preferably carried out in the 200 to 300 bar range. Hydrogen pressures of 220 to 260 bar are particularly preferred.

15 The hydrogenation in step ii) is preferably carried out in the presence of a solvent. Alcoholic compounds, especially low molecular weight primary alkanols, such as methanol and/or ethanol, are particularly suitable solvents. The quantity ratio of aldehyde to solvent in step ii) of the process according to the invention is basically not critical although ratios by  
20 volume of aldehyde to solvent of 10:1 to 1:10 are preferred, a range of 3:1 to 1:1 being particularly preferred.

The copper/zinc catalysts to be used for the purposes of the invention are known from the prior art. They are prepared in accordance with **DE-A-42 42 466** by adding alkali metal carbonate compounds to  
25 aqueous solutions containing water-soluble copper(II) and zinc(II) salts up to a pH value of 6 to 10, removing and drying the deposit formed, calcining the dried catalyst for 1 to 60 minutes at temperatures of 400 to 600°C and then converting the calcined catalyst into particulate form. Further information on the production of the copper/zinc catalysts can be found in  
30 **DE-A-42 42 466**, page 3, lines 13 to 34.

In order substantially to avoid further hydrogenation of the target product (I) to secondary products, it has proved to be favorable in the continuous reaction in a fixed-bed reactor to adjust the volumetric flow rate of the aldehyde to LHSV values which are preferably in the range from 0.3 to 3.0 h<sup>-1</sup> and more particularly in the range from 0.6 to 1.2 h<sup>-1</sup>. The LHSV value (liquid hourly space velocity) is understood from the literature to be the volumetric flow rate of the liquid, based on the volume of the solid catalyst. The LHSV values mentioned herein are based solely on the aldehyde, i.e. the solvent optionally used is disregarded.

The circulating gas volume is adjusted to values of 1 to 2 Dm<sup>3</sup>/h ("pressure cubic meters per hour"). By circulating gas volume is meant: m<sup>3</sup> circulating gas per hour for a reactor pressure of 250 to 300 bar. This parameter is measured in the pressure range of the reactor used (cf. Example 3 of the present application and the associated Fig. 1) after the gas circulation pump by means of a turbine.

For the purposes of the invention, the volumetric flow rate is normally adjusted to GHSV values in the range from 200 to 1,000 h<sup>-1</sup> and preferably to GHSV values in the range from 250 to 500 h<sup>-1</sup>. The GHSV value (gaseous hourly space velocity) is understood from the literature to be the volumetric flow rate of the carrier gas, based on the volume of the solid catalyst.

## Examples

25

### 1. Substances used

#### 1.1. For the aldol condensation

$\alpha$ -campholene aldehyde: 85% (Glidco)

propionaldehyde: 98% (Riedel-de-Häen)

30 KF on Al<sub>2</sub>O<sub>3</sub>: 240 g basic aluminium oxide were suspended in 320 g of a

50% aqueous potassium fluoride solution and then concentrated to dryness in a water jet vacuum in a rotary evaporator. The catalyst was then dried for 4 hours at 130°C/50 mbar.

5                    **1.2. For the reduction of the unsaturated aldehyde**

Copper/zinc catalyst: The copper/zinc catalyst used was prepared in accordance with Example A) of DE-A-42 42 466 using copper(II) nitrate trihydrate, zinc(II) nitrate hexahydrate and sodium carbonate.

10

**2. The reactions**

**2.1. Aldol condensation**

**Example 1**

Quantities used:

3.04 g (20 moles)  $\alpha$ -campholene aldehyde

15    4.64 kg (80 moles) propionaldehyde

400 g basic aluminium oxide charged with 40% potassium fluoride.

Reaction procedure:

1.5 kg of a mixture (molar ratio 1:4) of campholene aldehyde and  
20    propionaldehyde was introduced into a 10-liter glass reactor. 400 kg of KF  
on  $\text{Al}_2\text{O}_3$  were added in portions under nitrogen (5 l/h) with vigorous stirring  
and cooling, the temperature of the reaction mixture being kept between 40  
and 50°C. The remaining 6.2 kg of the aldehyde mixture were then  
continuously added under nitrogen with vigorous stirring at a rate of 2 liters  
25    per hour. The reaction was exothermic and was kept by cooling at 40°C.  
After the addition, the mixture was stirred overnight at 50°C, the  
campholene aldehyde reacting off completely.

Working up:

30                    To remove the catalyst, the reaction mixture was pumped into a 2-



liter pressure nutsche and filtered under 5 bar nitrogen. The filter cake was briefly washed with 0.5 liter of isopropanol. The crude product was returned to the reactor and ca. 270 g organic phase and 22 g water phase were distilled off at atmospheric pressure and at bottom temperatures of up to 150°C. The residue of 5.1 kg left in the reaction vessel was washed twice with 2 liters of saturated sodium sulfate solution. The residue of 5 kg remaining was further processed as a crude product (the content of 2-methyl-(2,2,3-trimethylcyclopent-3-en-1-yl)-but-2-en-1-al was found by gas chromatography to be 43%).

10

**Example 2****Quantities used:**3.04 kg (20 moles)  $\alpha$ -campholene aldehyde

2.9 kg (50 moles) propionaldehyde

15 170 + 85 g (3 moles) piperidine

120 + 60 g (3 moles) glacial acetic acid

2 kg toluene

**Reaction procedure:**

20 3.04 kg of campholene aldehyde and 2 kg of toluene were introduced into a 10-liter glass reactor and 2.9 kg of propionaldehyde, 170 g of piperidine and 120 g of glacial acetic acid were added with stirring at room temperature. The mixture was then refluxed for 4 hours on a water separator, 680 ml of water of reaction being removed from the circuit.

25 Analysis of a sample of the reaction mixture by gas chromatography revealed a percentage content of 15% of unreacted educt. Accordingly, another 85 g of piperidine and 60 g of glacial acetic acid were added. After refluxing for another hour, another 120 g of water were removed from the circuit and the educt was completely reacted.

30

Working up:

After 1.9 kg of toluene had been distilled off, the reaction mixture was washed twice with 2 liters of water. The organic phase of 6.24 kg was distilled in a 30 cm packed column (boiling point 88-102°C/0.1 mbar), 3.27  
5 kg of a yellowish colored product (gas-chromatographic purity 85%) being obtained (85% of the theoretical).

**2.2. Reduction**

**Example 3** (invention)

10 Apparatus:

A jacketed high-pressure reactor filled with a Cu/Zn catalyst was used. It was connected to the following units: high-pressure product pump, heater, cooler, separator and gas circulation pump. The heat carrier circuit was controlled by a temperature-controllable apparatus. The layout of the  
15 apparatus used is schematized in Fig. 1.

List of reference numerals in Fig. 1

- |    |   |   |
|----|---|---|
|    | 1 | educt (crude product of the aldol condensation of Example 2) / methanol |
| 20 | 2 | high-pressure product pump  |
|    | 3 | heater  |
|    | 4 | reactor (jacketed)  |
|    | 5 | heat carrier oil  |
|    | 6 | cooler  |
| 25 | 7 | separator   |
|    | 8 | gas circulation pump  |
|    | 9 | hydrogen supply ("fresh H <sub>2</sub> ")                               |

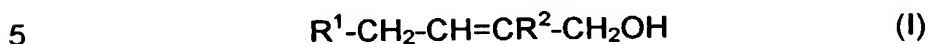
Quantities used:

- |    |  |
|----|--|
| 30 | 24.7 kg crude product of the aldol condensation of Example 2 (= educt) |
|----|--|

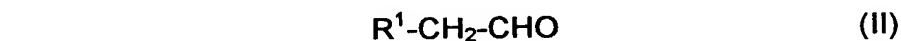
After it had been filled with the catalyst, the reactor was closed and tested for leaks with 250 bar hydrogen pressure. The catalyst was then activated by continuous introduction of hydrogen under a reactor pressure of 50 bar N<sub>2</sub> and at a temperature increased by 5°C per hour, a final temperature of 200°C being established. The circulating gas volume was kept at 1.5 Dm<sup>3</sup>/h. The end of activation of the catalyst, as reflected in an H<sub>2</sub> content in the circulating gas of more than 5%, i.e. the catalyst did not take up any more hydrogen, was followed by gas exchange in the reactor. To carry out the hydrogenation process, 250 bar hydrogen was introduced into the reactor after the complete expansion of hydrogen and the catalyst bed was adjusted to 50-55°C through the hydrogen, reactor entry and heat carrier temperature. The circulating gas volume was 2 Dm<sup>3</sup>/h. After the operating parameters had stabilized, the addition of a mixture of 2 parts by volume of the crude product of the aldol condensation of Example 2 (= educt) and 1 part by volume of methanol (= solvent) was started at 10 l/h, rising gradually to 40 l/h. After all the mixture had been added, the educt/hydrogen mixture showed a reactor entry temperature and heat carrier oil exit temperature of 55°C. The exothermy in the reactor was 5 to 10°C. After cooling, the hydrogenation product and the hydrogen were separated in a separator, the hydrogen was fed to the gas circulation pump and the end product was removed through an automatic expansion system. The crude product obtained in this way was then characterized by gas chromatography. It contained 86% of the required valuable product, 12% of a perfumistically attractive accompanying product and 1.8% of unreacted educt. Hardly any of the secondary products formed, for example, at higher temperatures or in batch operation were detected.

**CLAIMS**

1. A process for the production of alkyl-substituted butenols corresponding to general formula (I):



in which  $\text{R}^1$  is a saturated or olefinically unsaturated alkyl or cycloalkyl group containing 4 to 16 carbon atoms which may optionally be substituted by an alkyl, cycloalkyl, aryl or alkaryl group, with the proviso that this  
10 substituent contains at most 12 carbon atoms, and  $\text{R}^2$  is hydrogen or an alkyl group containing 1 to 6 carbon atoms,  
by reacting aldehydes corresponding to formula (II):



in which  $\text{R}^1$  has the same meaning as in formula (I), with the corresponding lower aldehydes and subsequently reducing the unsaturated aldehydes obtained,

- 20 i) the aldol condensation being carried out in an inert organic solvent and  
(ii) the reduction of the unsaturated aldehydes being carried out in the presence of an optionally calcined copper/zinc catalyst,  
characterized in that the reduction in step ii) is carried out continuously under isothermal conditions at temperatures of 45 to 60°C and under a  
25 hydrogen pressure of 1 to 300 bar.

2. A process as claimed in claim 1, characterized in that the aldol condensation is carried out in a nonpolar organic solvent which forms an azeotrope with water.

3. A process as claimed in claim 1 or 2, characterized in that the aldol  
30 condensation is carried out in the presence of an ammonium salt of an

organic acid as catalyst.

4. A process as claimed in any of claims 1 to 3, characterized in that  $R^2$  in formula (I) is a methyl group.

5. A process as claimed in claim 4, characterized in that propionaldehyde is used in a 2.5 to 10-fold molar excess, based on the aldehyde (II), in step i).

6. A process as claimed in any of claims 1 to 5, characterized in that  $R^1$  is a 4-(2,2,3-trimethylcyclopent-3-en-1-yl) group.

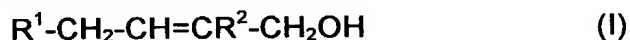
7. A process as claimed in any of claims 1 to 6, characterized in that an organic solvent selected from the group consisting of toluene, xylene, benzene, cyclohexane and methyl cyclohexane is used in step i).

8. The use of the alkyl-substituted butenols of formula (I), in which  $R^1$  is a saturated or olefinically unsaturated alkyl or cycloalkyl group containing 4 to 16 carbon atoms which may optionally be substituted by an alkyl, cycloalkyl, aryl or alkaryl group, with the proviso that this substituent contains at most 12 carbon atoms, and  $R^2$  is hydrogen or an alkyl group containing 1 to 6 carbon atoms, produced by the process claimed in any of claims 1 to 7 as perfumes.

9. The use claimed in claim 8 in cosmetic preparations, technical products or alcohol-based perfumery.

## ABSTRACT OF THE DISCLOSURE

Alkyl-substituted butenols having the formula (I):



wherein  $\text{R}^1$  is a saturated or olefinically unsaturated alkyl or cycloalkyl group having from 4 to 16 carbon atoms and wherein  $\text{R}^1$  is optionally substituted by an alkyl, cycloalkyl, aryl or alkaryl having up to 12 carbon atoms;  $\text{R}^2$  is hydrogen or an alkyl group having from 1 to about 6 carbon atoms are produced by a process which comprises: (1) reacting an aldehyde of the formula (II):



wherein  $\text{R}^1$  has the same meaning as in formula (I), with the corresponding lower aldehyde to form an unsaturated aldehyde in an inert organic solvent; (2) continuously contacting an optionally calcined copper/zinc catalyst with the unsaturated aldehyde under isothermal conditions at temperatures of from about 45 to about 60°C and under a hydrogen pressure of from 1 to about 300 bar.

#5

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# DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket Number

H 4193 PCT/US

First Named Inventor

FRISENHAGEN, Lothar

## COMPLETE IF KNOWN

Application Number

10/088,385

Filing Date

08/12/2002

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**METHOD FOR PRODUCING ALKYL-SUBSTITUTED BUTENOLS**

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY)

**09/08/2000**

as United States Application Number or PCT International

Application Number

**PCT/EP00/08772**

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application Number(s) | Country | Foreign Filing Date (MM/DD/YYYY) | Priority Not Claimed     | Certified Copy Attached?<br>YES NO                           |
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## DECLARATION

Page 2

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §365(c) of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112.1 acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

| U.S. Parent Application Number | PCT Parent Number | Parent Filing Date (MM/DD/YYYY) | Parent Patent Number (if applicable) |
|--------------------------------|-------------------|---------------------------------|--------------------------------------|
|                                | PCT/EP00/08772    | 09/08/2000                      |                                      |

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

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☒ List Attorney(s) and/or agent(s) name and registration number below:

| Name              | Registration Number | Name                  | Registration Number |
|-------------------|---------------------|-----------------------|---------------------|
| John E. Drach     | 32,891              | Aaron R. Ettelman     | 42,516              |
| Steven J. Trzaska | 36,296              | Henry E. Millson, Jr. | 18,980              |

☐ Additional attorney(s) and/or agent(s) named on a supplemental sheet attached hereto.

Please direct all correspondence to:

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|         |               |     |              |
|---------|---------------|-----|--------------|
| Name    | John E. Drach |     |              |
| Address |               |     |              |
| Address |               |     |              |
| City    | State         | ZIP |              |
| Country | Telephone     | Fax | 610-278-4971 |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Name of Sole or First Inventor:

☐ A petition has been filed for this unsigned

|            |        |                |  |             |              |                 |  |
|------------|--------|----------------|--|-------------|--------------|-----------------|--|
| Given Name | Lothar | Middle Initial |  | Family Name | Friesenhagen | Suffix e.g. Jr. |  |
|------------|--------|----------------|--|-------------|--------------|-----------------|--|

|                      |   |      |          |
|----------------------|---|------|----------|
| Inventor's Signature |  | Date | 24.04.02 |
|----------------------|---|------|----------|

|                 |             |       |     |         |         |             |         |
|-----------------|-------------|-------|-----|---------|---------|-------------|---------|
| Residence: City | Duesseldorf | State | DEU | Country | Germany | Citizenship | Germany |
|-----------------|-------------|-------|-----|---------|---------|-------------|---------|

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|------|-------------------|-------|--|-----|--|---------|---------|---------------------|--|
| City | 40589 Duesseldorf | State |  | Zip |  | Country | Germany | Applicant Authority |  |
|------|-------------------|-------|--|-----|--|---------|---------|---------------------|--|

☒ Additional inventors are being named on supplemental sheet(s) attached hereto



Type a plus sign (+) inside this box

1.0798385 081202  
H 4193 PCT/US

## DECLARATION

ADDITIONAL INVENTOR(S)  
Supplemental Sheet

Name of Additional Joint Inventor, if any:



A petition has been filed for this unsigned inventor

|                      |                     |                |     |             |         |                     |           |
|----------------------|---------------------|----------------|-----|-------------|---------|---------------------|-----------|
| Given Name           | Stephan             | Middle Initial |     | Family Name | Heck    | Suffix e.g. Jr.     |           |
| Inventor's Signature | <i>Stephan Heck</i> |                |     |             |         | Date                | 8.04.2002 |
| Residence: City      | Pulheim             | State          | DEX | Country     | Germany | Citizenship         | Germany   |
| Post Office Address  | Patriziusstrasse 12 |                |     |             |         |                     |           |
| Post Office Address  |                     |                |     |             |         |                     |           |
| City                 | 50259 Pulheim       | State          |     | Zip         |         | Country             | Germany   |
|                      |                     |                |     |             |         | Applicant Authority |           |

Name of Additional Joint Inventor, if any:



A petition has been filed for this unsigned inventor

|                      |                      |                |     |             |         |                     |           |
|----------------------|----------------------|----------------|-----|-------------|---------|---------------------|-----------|
| Given Name           | Norbert              | Middle Initial |     | Family Name | Klein   | Suffix e.g. Jr.     |           |
| Inventor's Signature | <i>Norbert Klein</i> |                |     |             |         | Date                | 6.03.2002 |
| Residence: City      | Mettmann             | State          | DEX | Country     | Germany | Citizenship         | Germany   |
| Post Office Address  | Roemerstrasse 1h     |                |     |             |         |                     |           |
| Post Office Address  |                      |                |     |             |         |                     |           |
| City                 | 40822 Mettmann       | State          |     | Zip         |         | Country             | Germany   |
|                      |                      |                |     |             |         | Applicant Authority |           |

Name of Additional Joint Inventor, if any:



A petition has been filed for this unsigned inventor

|                      |                       |                |     |             |         |                     |           |
|----------------------|-----------------------|----------------|-----|-------------|---------|---------------------|-----------|
| Given Name           | Thomas                | Middle Initial |     | Family Name | Markert | Suffix e.g. Jr.     |           |
| Inventor's Signature | <i>Thomas Markert</i> |                |     |             |         | Date                | 7.03.2002 |
| Residence: City      | Monheim               | State          | DEX | Country     | Germany | Citizenship         | Germany   |
| Post Office Address  | Lottenstrasse 55      |                |     |             |         |                     |           |
| Post Office Address  |                       |                |     |             |         |                     |           |
| City                 | 40789 Monheim         | State          |     | Zip         |         | Country             | Germany   |
|                      |                       |                |     |             |         | Applicant Authority |           |

Name of Additional Joint Inventor, if any:



A petition has been filed for this unsigned inventor

|                      |                      |                |     |             |         |                     |                |
|----------------------|----------------------|----------------|-----|-------------|---------|---------------------|----------------|
| Given Name           | Gerrit               | Middle Initial |     | Family Name | Pelzer  | Suffix e.g. Jr.     |                |
| Inventor's Signature | <i>Gerrit Pelzer</i> |                |     |             |         | Date                | March, 06 2002 |
| Residence: City      | Duesseldorf          | State          | DEX | Country     | Germany | Citizenship         | Germany        |
| Post Office Address  | Am Baerenkamp 4a     |                |     |             |         |                     |                |
| Post Office Address  |                      |                |     |             |         |                     |                |
| City                 | 40589 Duesseldorf    | State          |     | Zip         |         | Country             | Germany        |
|                      |                      |                |     |             |         | Applicant Authority |                |



Additional inventors are being named on supplemental sheet(s) attached hereto

Type a plus sign (+) inside this box

1009335 001202

H 4193 PCT/US

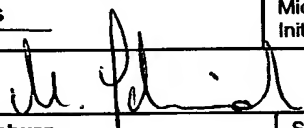
## DECLARATION

ADDITIONAL INVENTOR(S)  
Supplemental Sheet

Name of Additional Joint Inventor, if any:

☐ A petition has been filed for this unsigned inventor

|            |        |                |  |             |           |                 |  |
|------------|--------|----------------|--|-------------|-----------|-----------------|--|
| Given Name | Markus | Middle Initial |  | Family Name | Schneider | Suffix e.g. Jr. |  |
|------------|--------|----------------|--|-------------|-----------|-----------------|--|

|                      |   |      |          |
|----------------------|---|------|----------|
| Inventor's Signature |  | Date | 04/25/02 |
|----------------------|---|------|----------|

|                 |          |       |    |         |         |             |         |
|-----------------|----------|-------|----|---------|---------|-------------|---------|
| Residence: City | Duisburg | State | DE | Country | Germany | Citizenship | Germany |
|-----------------|----------|-------|----|---------|---------|-------------|---------|

Post Office Address Zum Holzenberg 9

Post Office Address

|      |                |       |  |     |  |         |         |                     |  |
|------|----------------|-------|--|-----|--|---------|---------|---------------------|--|
| City | 47279 Duisburg | State |  | Zip |  | Country | Germany | Applicant Authority |  |
|------|----------------|-------|--|-----|--|---------|---------|---------------------|--|

Name of Additional Joint Inventor, if any:

☐ A petition has been filed for this unsigned inventor

|            |  |                |  |             |  |                 |  |
|------------|--|----------------|--|-------------|--|-----------------|--|
| Given Name |  | Middle Initial |  | Family Name |  | Suffix e.g. Jr. |  |
|------------|--|----------------|--|-------------|--|-----------------|--|

|                      |  |      |  |
|----------------------|--|------|--|
| Inventor's Signature |  | Date |  |
|----------------------|--|------|--|

|                 |  |       |  |         |  |             |  |
|-----------------|--|-------|--|---------|--|-------------|--|
| Residence: City |  | State |  | Country |  | Citizenship |  |
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| City |  | State |  | Zip |  | Country |  | Applicant Authority |  |
|------|--|-------|--|-----|--|---------|--|---------------------|--|

Name of Additional Joint Inventor, if any:

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|            |  |                |  |             |  |                 |  |
|------------|--|----------------|--|-------------|--|-----------------|--|
| Given Name |  | Middle Initial |  | Family Name |  | Suffix e.g. Jr. |  |
|------------|--|----------------|--|-------------|--|-----------------|--|

|                      |  |      |  |
|----------------------|--|------|--|
| Inventor's Signature |  | Date |  |
|----------------------|--|------|--|

|                 |  |       |  |         |  |             |  |
|-----------------|--|-------|--|---------|--|-------------|--|
| Residence: City |  | State |  | Country |  | Citizenship |  |
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| City |  | State |  | Zip |  | Country |  | Applicant Authority |  |
|------|--|-------|--|-----|--|---------|--|---------------------|--|

Name of Additional Joint Inventor, if any:

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|            |  |                |  |             |  |                 |  |
|------------|--|----------------|--|-------------|--|-----------------|--|
| Given Name |  | Middle Initial |  | Family Name |  | Suffix e.g. Jr. |  |
|------------|--|----------------|--|-------------|--|-----------------|--|

|                      |  |      |  |
|----------------------|--|------|--|
| Inventor's Signature |  | Date |  |
|----------------------|--|------|--|

|                 |  |       |  |         |  |             |  |
|-----------------|--|-------|--|---------|--|-------------|--|
| Residence: City |  | State |  | Country |  | Citizenship |  |
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|      |  |       |  |     |  |         |  |                     |  |
|------|--|-------|--|-----|--|---------|--|---------------------|--|
| City |  | State |  | Zip |  | Country |  | Applicant Authority |  |
|------|--|-------|--|-----|--|---------|--|---------------------|--|

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